

MACROSCOPIC ENRICHMENT OF ^{12}C BY A HIGH-POWER MECHANICALLY Q-SWITCHED CO_2 LASER

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Abstract. The isotope selective multiphoton dissociation of CHClF_2 in a multipass refocusing Herriott cell was used to enrich more than 4 moles of chlorodifluoromethane to 99.99 % of ^{12}C isotopic purity. It is the largest isotope quantity ever separated by a laser process. A cw excited mechanically Q-switched CO_2 laser, which delivers 16 mJ pulses at 5 kHz was used. The enrichment controlled by a mass-spectrometer and guided by PC was run with a rate of 25 g ^{12}C per 24 hours.

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Introduction

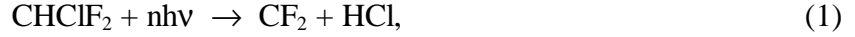
Natural carbon contains 1.11 % ^{13}C atoms. In diamond crystals, they behave like undesirable defects within the ^{12}C lattice. It has already been shown [1] that even at room temperature pure ^{12}C diamond crystals have a 1.5 times better heat conductivity than the best "normal" diamonds. Better heat conductivity has been recently demonstrated also for chemical vapour deposited polycrystalline ^{12}C diamond films [2]. ^{12}C diamonds have been used successfully as a heat sink substrate in microelectronics [3]. Other applications of ^{12}C are solvents for NMR spectroscopy [4] and the preparation of large, isotopically pure molecules (e.g. fullerenes) which could be easier analysed by mass spectrometry.

At present, nearly all ^{12}C is produced in the US by means of the low temperature distillation of CO , which takes place in a sequence of large liquid nitrogen cooled columns. A given distillation column is good only for one fixed degree of enrichment and it must be filled with a minimum quantity of CO . Then it takes several months to reach the separation equilibrium. In this work, we present a competitive and compact technique for the ^{12}C enrichment, which is more flexible in these respects.

Multiphoton dissociation of CHClF_2

The isotopically selective multiphoton dissociation (MPD) of polyatomic molecules by short IR laser pulses has been considered a promising isotope separation method for a long time [5,6]. However early attempts (e.g. a 100 kg ^{13}C /year isotope plant [5]) failed because of poor laser reliability, high cost of TEA CO_2 laser photons and the difficulty to use them efficiently. Only during the last years, a real progress has been achieved and macroscopic quantities of Si isotopes [7] and ^{13}C [8] have been separated by laser.

A very suitable starting material for carbon isotopes separation by MPD is CHClF_2 [9,10]. It dissociates when excited by a CO_2 laser at a wavelength of $\lambda=9.6 \mu\text{m}$ and keeps a high dissociation probability and isotope selectivity up to pressures of several tens of mbar. The MPD process for this molecule is well investigated and optimised (see e.g. [11] and references there). After the dissociation of CHClF_2 , the formed difluorocarbene dimerizes spontaneously as follows:



Under appropriate conditions, including a suitable laser wavelength around $9.6 \mu\text{m}$, the stable product C_2F_4 is enriched with ^{13}C and the starting material with ^{12}C . It is convenient for our purpose to characterise the process by an isotope selectivity S , which is equal to the ratio of dissociation probabilities of $^{13}\text{CHClF}_2$ and $^{12}\text{CHClF}_2$, an enrichment factor e_{12} , and by an equivalent dissociation volume u_{13} . The latter, multiplied by $^{13}\text{CHClF}_2$ concentration, is the number of the ^{13}C containing molecules converted per pulse. The enrichment factor e_{12} is the factor by which the $^{12}\text{C}/^{13}\text{C}$ ratio has been increased in the enriched CHClF_2 relative to the initial abundance ratio and a value of 100 means 99.99 % pure $^{12}\text{CHClF}_2$.

Operating the enrichment as a continuous process, the irradiated gas is uninterruptedly exchanged by fresh chlorodifluoromethane in such a way, that e_{12} and the pressure in the reaction cavity remain constant. The ^{12}C enrichment rate for this case is obtained from the material balance equations for the molecular concentrations (see Appendix 1),

$$R_{12} = fu_{13}\rho_{12} \left(\frac{1}{e_{12}} - \frac{1}{S} \right), \quad (3)$$

where f is the laser pulse repetition frequency and ρ_{12} is the number density of $^{12}\text{CHClF}_2$ fed into the cavity. From this formula, it follows that the selectivity S should be high compared to the desired value of e_{12} . Otherwise, the continuous flow of the fresh gas, which is necessary to replace the converted molecules, would keep the enrichment factor small. S can be as high as 500 for 9P(28) CO_2 laser line. However the equivalent dissociation volume u_{13} for this wavelength is very small ($u_{13}S \approx \text{const}$, [11]) and the laser oscillation is not efficient. Our initial attempts to run the continuous process showed a mass enrichment rate of about $1 \text{ g } ^{12}\text{C}/\text{day}$.

Much higher rates R_{12} are inherent in a batch process. In this case, all the gas is exchanged periodically when the necessary enrichment is achieved, so moderate selectivity, e.g. $S \approx 50$, is acceptable. For the batch process (see Appendix 2)

$$R_{12} = \frac{fu_{13}\rho_{12}}{\sqrt[e_{12}]{e_{12}} \ln(e_{12})}. \quad (4)$$

The duration T of a single batch cycle is proportional to the gas volume V of the batch:

$$T = \frac{V \ln(e_{12})}{f u_{13}}. \quad (5)$$

Multipass cell

We carried out the dissociation in a refocusing multipass cell of the Herriott type. It helped to maintain a high intensity over a long pathlength. Typically several meters are required for full absorption of all photons. This cell consists of two coaxial mirrors positioned between concentric and confocal configuration [12]. The laser beam is injected off-axially through a small hole near the periphery of one of the mirrors and travels between them in a zigzag manner being refocused in every transit. Such a cell has already been successfully used by us for an investigation of the CHClF_2 MPD [13] and the demonstration of a macroscopic ^{13}C separation [8].

The dissociation probability is a non-linear function of the IR energy density Φ . The region of quadratic dependence is the best choice for dissociation in a focused beam [14]. In the case of CHClF_2 irradiated by the 9P(22) CO_2 laser line, the optimum energy density is $\Phi=10 \text{ J/cm}^2$ [13]. In combination with an available pulse energy E this value determines the focal area and hence the Rayleigh length L_R . This in turn fixes the length of the cell L and the radius of curvature R of the refocusing mirrors [13]. In our case the parameters are as follows: $E=16 \text{ mJ}$, $L=123 \text{ mm}$, $L/L_R=3.5$, $R=70 \text{ mm}$. With appropriate adjustment of the cell 44 laser beam transits have been achieved compared to only 4 transits in [15] or 6 passes for the laser intracavity configuration in [16].

Laser

A detailed description of the dc excited oscillator-amplifier system is given in [17]. Q-switching is done by a fast rotating chopper disk interrupting the focal line within a hollow conical mirror telescope. As this configuration is very similar to a retro-reflector, alignment is easy and uncritical. Even within a long-term run no realignment is required. A low dispersion grating (30 grooves/mm) in Littrow arrangement enables simultaneous oscillation on two or three adjacent lines simultaneously, which is favourable for the multiphoton excitation [11,18]. The laser provides pulses with an energy of 15...22 mJ, a pulse duration (FWHM) of 200...250 ns and a beam divergence of 1.15 times the diffraction limit at a repetition rate of 2...12 kHz. In the described experiment we kept f fixed to 5 kHz.

Process control and gas handling scheme

The irradiation cell is a part of the gas circulation system, which is shown schematically in Fig. 1. The gas mixture of CHClF_2/He is transversely blown through the irradiation cell at a speed of 20 m/s. The control of the dissociation parameters, of the laser and the gas handling is automated. When the laser beam is switched on, the CHClF_2 molecules containing ^{13}C are depleted more and more. This is monitored by a quadrupole mass-spectrometer. Five mass signals, being necessary for precise enrichment and isotope selectivity control (see Table), are measured every 2 seconds.

As soon as the desired value e_{12} is reached, the laser beam is interrupted. The unconverted $^{12}\text{CHClF}_2$ molecules together with the dissociation products C_2F_4 and HCl are withdrawn by a circulation pump and condensed in a cooled trap, whereas helium stays there as a gaseous supply for the next fill. The laser power, temperature and pressure in the trap are also controlled by the computer. Failures can be recognised, and an emergency shutdown is carried out in such a case.

Compared to the production of ^{13}C [8], the control algorithm is by far simpler because the batch-type process requires no feedback to establish a stationary state of the system. However one has to avoid very carefully any dead volume, i.e. volume which exchanges its gas only slowly with the irradiated gas. This can be e.g. the space between valves and the circulation system. With the set-up shown in Fig. 1 it is possible to reach an enrichment factor of $e_{12} \geq 200$. By adding a buffer volume into the gas circulation system much higher e_{12} values become conceivable.

Results

The enrichment experiment continued up to 6-10 hours per day for two weeks. The irradiated gas was renewed, when the measured enrichment factor reached $e_{12}=200$. Such a high value is already at the detection limit of our mass spectrometer. A later analysis of the enriched gas with a high precision gas-chromatograph mass-spectrometer combination showed $e_{12} \geq 100$. The duration of one irradiation cycle was about 2 min with an isotope selectivity $S \approx 50$.

Optimisation of the irradiated gas mixture has been done. The best mixture which is 30 mbar $\text{CHClF}_2/180$ mbar He, is very similar to the optimum mixture for a single pass dissociation with 20 mbar/180 mbar, providing the maximum value of u_{13} [11]. Increasing the chlorodifluoromethane pressure supplies more gas for the dissociation by the increase of the particle density but the converted volume u_{13} drops. The measured mass enrichment rate was 25 g $^{12}\text{C}/24$ hours at 30 mbar and 20 g $^{12}\text{C}/24$ hours at 20 mbar CHClF_2 . The latter value is in good agreement with a theoretical estimation based on equation (4) and the dissociation parameters measured for such a mixture in [13] (see Fig. 2). In total, 50 g of ^{12}C were enriched to more than 99.99 %.

The enriched chlorodifluoromethane (360 g) which was accumulated in the cold trap was later separated from C_2F_4 (10.4 g) and HCl (7.6 g) by a low temperature distillation in a small (1.1 m in height) laboratory column. CHClF_2 is a good starting material for the synthesis of different chemical compounds. An experiment to transform it into CF_4 is under preparation now.

Discussion

Our results show that the multiphoton dissociation of CHClF_2 by CO_2 laser pulses is an attractive method of ^{12}C enrichment. The mass enrichment rate at $e_{12}=100$ (99.99 % ^{12}C) is 25 times higher than for laser enrichment of ^{13}C up to 50% [8]. A further scaling is possible with the laser pulse energy and repetition rate.

At a repetition rate of 5 kHz and with the Herriott cell employed ($L/L_R=3.5$) the average intensity of every single beam at the cell mirrors was $I \approx 6 \text{ kW/cm}^2$ and the peak intensity (at the centre of a single spot) of about 20 MW/cm^2 . Higher intensity would lead to a fairly rapid (within several tens of hours) degradation of the gold coated copper mirrors. Thus a smaller I is desirable. The reduced damage threshold is connected with photochemical deposition of teflon-like material at the mirror surfaces. Special tests showed that the average intensity I is the main parameter determining the rate of degradation. To reduce it, we have developed a computer controlled beam deflection system. It allows to increase the repetition rate at least two times.

The scaling of the production rate with the pulse energy E is straightforward. In order to maintain the optimum energy density $\Phi=10 \text{ J/cm}^2$, adjustment of the focal area proportional to E is necessary which means milder focusing and a Rayleigh length $L_R \propto E$. At the same time, the length of the cell should be increased by the same factor. Thus the equivalent dissociation volume u_{13} will initially increase $\propto E^2$, until the beam path length is comparable to the absorption length in the gas. Then one would observe a growth of $R_{12} \propto E$.

The theoretical scaling curves are shown in Fig. 2. At a pulse energy of 150 mJ and with 5 kHz repetition rate, the expected enrichment rate is more than 1000 g/24 hours. Estimations show that such parameters are achievable with a 5 kW (cw) industrial CO₂ laser, modified for Q-switching, and a dissociation cell of 1 m length.

Utilising a state-of-the-art 5 kW laser module would reduce the photon cost 2-3 times compared to the presently used CO₂ laser based on an old 1 kW cw-output design. Due to the scaling law with laser pulse energy, the photons would be used more efficiently. Thus, the production cost would drop even 5 times. In any case it would be fairly below the actual market price.

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Appendix 1

Under the conditions of a continuous enrichment a volume flow F_{in} of fresh chlorodifluoromethane into the cell compensates the losses by dissociation and the quantity (F_{out}) removed from the irradiation cell:

$$F_{in} = (fu_{13} + F_{out})(1 - c_{13}) = (fu_{13} / S + F_{out})(1 - c_{12}), \quad (\text{A1.1})$$

where c_{12} , c_{13} are the dissociated fractions of $^{12}\text{CHClF}_2$ and $^{13}\text{CHClF}_2$ respectively, which define the enrichment factor,

$$e_{12} = \frac{1 - c_{12}}{1 - c_{13}}. \quad (\text{A1.2})$$

From (A1.1, A1.2) and the condition $e_{12} \gg 1$ follows equation (3) for the continuous ^{12}C enrichment rate:

$$R_{12} = \rho F_{out} = fu_{13} \rho \left(\frac{1}{e_{12}} - \frac{1}{S} \right). \quad (\text{A1.3})$$

Appendix 2

During the batch cycle both the numbers of $^{13}\text{CHClF}_2$ and $^{12}\text{CHClF}_2$ molecules decrease and e_{12} increases exponentially:

$$N_{12} = N_{12}^0 \exp\left(-\frac{ftu_{13}}{SV}\right), \quad (\text{A2.1})$$

$$N_{13} = N_{13}^0 \exp\left(-\frac{ftu_{13}}{V}\right), \quad (\text{A2.2})$$

$$e_{12} = \frac{N_{12}}{N_{12}^0} \frac{N_{13}^0}{N_{13}} = \exp\left[\frac{ftu_{13}}{V} \left(1 - \frac{1}{S}\right)\right]. \quad (\text{A2.3})$$

Noting that $S \gg 1$, the duration T of the batch cycle is found to be

$$T = \frac{V \ln(e_{12})}{fu_{13}}. \quad (\text{A2.4})$$

The number of $^{12}\text{CHClF}_2$ molecules at the end of the batch is

$$N_{12}(T) = \frac{N_{12}^0}{\sqrt[e_{12}]{}}. \quad (\text{A2.5})$$

From (A2.4, A2.5) follows the formula (4) for the enrichment rate of the batch process:

$$R_{12} = \frac{fu_{13} \rho}{\sqrt[e_{12}]{\ln(e_{12})}}. \quad (\text{A2.6})$$

Table: Controlled mass signals and corresponding molecular fragments.

mass	fragment	molecule
52	$^{13}\text{CHF}_2$	CHClF_2
86	$^{12}\text{CH}^{35}\text{ClF}_2$	CHClF_2
81	$^{12}\text{C}_2\text{F}_3$	C_2F_4
82	$^{12}\text{C}^{13}\text{CF}_3$	C_2F_4
83	$^{13}\text{C}_2\text{F}_3$	C_2F_4

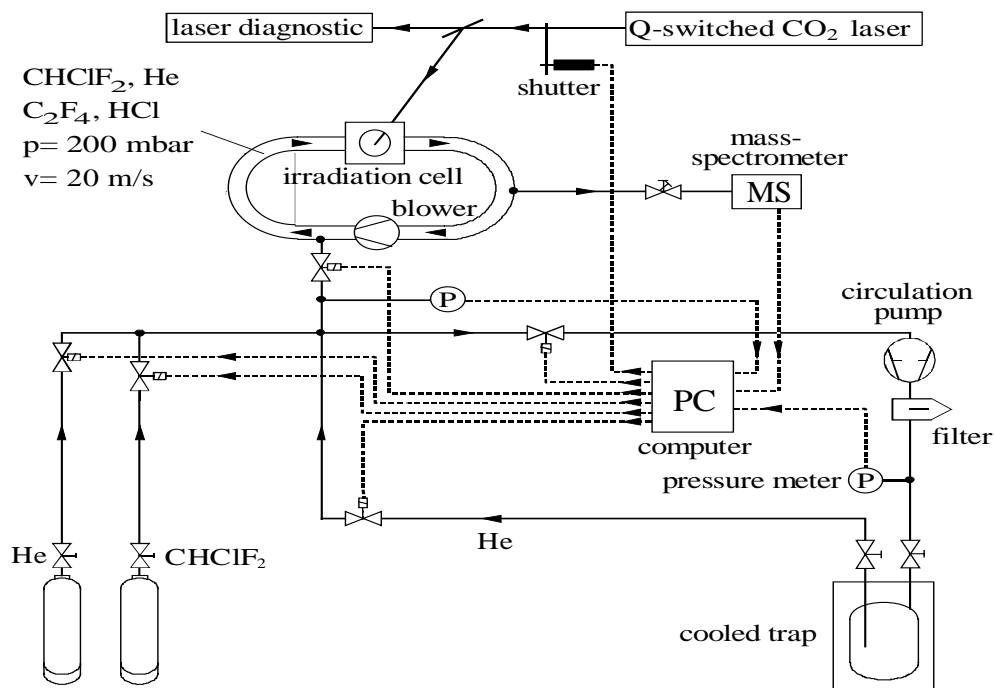


Fig. 1. Scheme of the gas flow and control system.

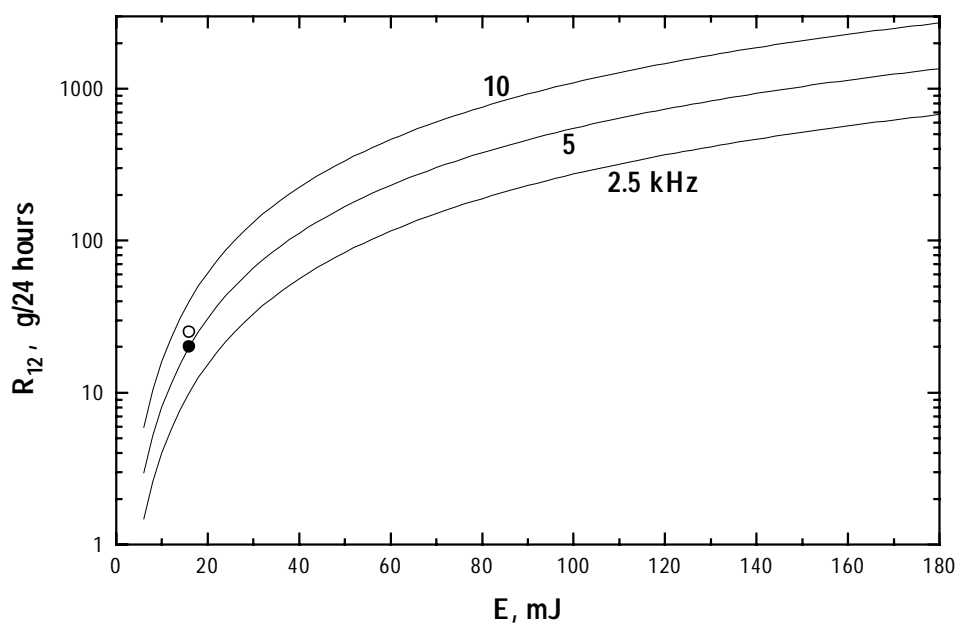


Fig. 2.

Fig. 2. Calculated mass enrichment rate of ^{12}C (up to 99.99 %) versus laser pulse energy at different repetition rates for a mixture of 20 mbar CHClF_2 + 180 mbar He, $\Phi=10 \text{ J/cm}^2$, $L=3.5 \cdot L_R$. Circles show the observed mass enrichment rate R_{12} at 20 (filled) and 30 (hollow circle) mbar CHClF_2 (+180 mbar He). $R_{12}=12 \cdot R_{12} \cdot 24 \cdot 3600 / N_A$, N_A is the Avogadro constant.